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Description

Fully closed, zero discharge, clean oxidizing pulping technology and process

Field of the invention

The invention relates to a process for a fully closed, zero discharge, clean oxidizing pulping technology and process. It is practically a process that involves a method with close-loop, self-cycling, non-acid, non-alkali, non-chlorine, non-anthraquinone, non-cooking, non-bleaching, non-draining and non-pollution.

Background of the invention

Short supply of papermaking materials is a problem faced by the pulping & papermaking in a long term and occurs not in a single district but in worldwide. Forest acts as the lung of earth that can absorb carbon dioxide and produce oxygen in addition to the effect on the conservation water resources, prevention of soil erosion, and adjustment of climate. And it has ecological and economic value. However, it is now decreasing at a rate of $700 \times 10^8 \text{m}^2$ yearly and tropical rain forest is being reduced at a rate of $50 \times 10^4 \text{m}^2$ per minute. If the illegal ruinous exploitation is not strictly restricted, with the increasing of the whole world population, human beings may have to face the dilemma of non-adequate oxygen to breathe 40 years later.

According to the China Forestry Statistical Yearbook compared with 1999, the decreasing rate of forest area in 2000 is: ten forestry ecological programs -12.9%, natural formed conservation program -10.7%, area of enclosure of the hillside for regeneration -6.33%, protection forest +24.75%, economic plantations -3.83% and forest of commercial timber -14.07%.

Based on cellulose chemistry, non-wood fiber materials can be categorized as: 1. the grass fiber materials 2. base fiber materials 3. cotton linters fiber materials 4. leaf fiber materials. And the holocellulose content is 48%-84%. The length of most non-wood fiber is longer than that of wood fiber and cellulose is main content used in papermaking. Cellulose extracted both from wood and non-wood materials can be used as supporting materials of paper and raw material of middle or high quality pulp. It is demonstrated that in the fiber of non-wood materials such as cotton stalk, all kinds of chemical components are similar to that of hard wood and soft wood. China is an agricultural country and also is a cotton-producing country. Annual resource that can compare favorably with wood is about 0.16 billion tons. During the "Ten-Five" plan, the major cotton-producing area of China is stabilized at 6 million hm^2 in 2010. There are 34.2 million tons high quality cotton stalks annually. Based on the data of textbook, output of cotton stalk pulp is 24.282 million tons. If the utilization ratio is 20%, the output is 4.856 million t/y, heretofore the utilization ratio of the annual resource resembled the hard wood is less than 1%. 0.235 billion tons fiber materials of non-wood can be extracted from cornstalk, wheat straw, rice straw (in accordance with year 2000 agriculture statistical yearbook, yield of them has already attained 0.47 billion tons). Now utilization ratio of the vast annual pulp materials is less than 5%. These annual resources are called agriculture green waste in America, and are called green annual resource in China.

In "Pulping Technology and Equipment" that published by China Light Industry Publishing House in year 2000, the content of holocellulose of various fiber materials tested with sodium is listed in table 1.

Table 1 unit: weight %

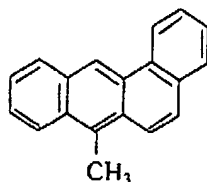
Materials	Production Place	Holocellulose	Materials	Production Place	Holocellulose
spruce	xiaoxinganli	73.0	Wheat straw	Hebei	71.3
korean pine	ng	69.6	Sugarcane	Guawngdon	75.6
populus	daxinganling	81.6	Chinese alpine g		76.7
xiaozuanyangica	henan	69.5	rush	Guangxi	66.4
bambusa oldhami	zhejiang	67.2	Sorghum stalk	Hebei	84.9
Bambusa	Guangdong	75.4	Corn stalk	Hebei	79.8
eduldoides	Hubei	76.6	Achnatherum	Jingxia	74.9
phragmites	Hubei	75.1	Deyounia	Heilongjiang	84.3
communis	Jiangsu	64.0	angstyolia	Sichuan	
miscanthus	Hebei		Chinese silvergrass		
sinensis					
gossypium					
hirsutum					
rice strew					

In "Cellulose Chemistry" that published by China Light Industry Publishing House in year 2001, data of cotton stalk materials chemical analysis (weight%) and average staple (mm) is listed in table 2.

Table 2

Part of cotton stalk	moisture	ash	extractive				Sodium chlorite holocellulose	Klaso n Lignin	Poly pento se	Pecti n	Avera ge fiber
			Cold water	Hot water	1%Na OH	Pheny l alcohol					
Cotton stalk peel	6.12	6.12	18.34	23.66	43.57	2.7	75.57	16.84	23.26	9.64	2.46
Cotton cane	7.87	2.05	3.71	5.02	21.36	1.68	76.32	21.31	18.07	1.42	1.08
Full cotton stalk	8.12	3.15	7.68	9.74	28.72	1.94	75.95	20.17	19.27	4.25	1.68

It is well-known that worldwide papermaking still uses the traditional process invented before 100 years in which strong acid, strong alkali, strong chlorine are used and black liquor is drained without restraint. The traditional process has seriously impacted the environment that humankind relies for existence. In recent years Anthraquinone is introduced in papermaking of Japan, India, Canada etc. Anthraquinone belongs to the fused polycyclic hydrocarbons of arenes. The fused polycyclic hydrocarbons have been confirmed to be the carcinogen. For instance, a carcinogen structure made of anthracene is as follows:



10-Methyl-1, 2-benzanthracene-(ethene)-1, 2-benzanthracene

The prohibition order of pulp bleaching with chemicals relate to chlorine was promulgated by Environmental Protection Agency (USA) in April 2000. More recently, 54% paper mills in the world are fixing their eyes on ClO_2 as the bleaching agent. Nevertheless, 91% ClO_2 may produce dioxine and other organic compounds, and the remained 9% Cl_2 is discharged to the atmosphere, which harm the environment that human beings rely on.

The oxidizing bleaching of pulp can date back to the 1950's. Oxygen was first found that it has bleaching ability by Soviet wood chemist Nikicic and Arim in 1952. Twelve years later, Magnesium salts are found to be able to avoid cellulose oxidation and degradation by French scientist Rebeve et al in 1964. Laboratories one after another were established in three countries (America, France and Sweden) in 1970. In the same year, the first chlorine dioxide bleaching plant of the world was constructed in Enstrd of South Africa. In 1972, ClO_2 bleaching plant with capacity of

12t/d was set up in America and was patented. But it was not industrialized due to the great loss of cellulose, high energy and water consumption and high production cost. Twenty-seven years later, Gerogelude Company in France (1999) and Prinsell Company in America (2001) successively used the combination of ClO_2 and O_3 bleaching. But chlorine pollution was not shaken off. Referring to the patent before March, 2002 of all over the world, the worldwide papermaking stand still as the seriously polluting cooking process with strong acid, strong alkali and strong chlorine, and stand still as the seriously polluting bleaching process with chlorine. Treatment of lignin chromophore stands still as traditional process of separation and degradation of lignin in 100 years before. For this reason, papermaking of the world has become the emphases object of the environment protection organization.

Pulp bleaching with ClO_2 and O_3 (CN1212310A) invented by France liquid air company was made public at March 31, 1999. Pulping of cornstalk and other non-wood fiber materials (CN1371439A) invented by America Carolina State University was made public at Sep 25, 2002. A method that produces pulp by non-wood and its preparation system equipment (CN1407172A) invented by Japan business corporation, a pollution-free pulping method (CN1198492) invented by Shandong Weichang Normal University, a pulping method without alkali (CN1229155) and a pulp bleaching electrochemical technology of polyoxometallate (CN1458075) were made public at April 2, 2003.

Referring to all above instruction patents, some are bleaching without chlorine, some are reducing the dosage of acid, alkali and chlorine, some are using ozone instead of chlorine, some are using alkali, anthraquinone and peroxide acid. Until March, 2002, there are no any plant can finish degradation of lignin without acid, alkali and no any plant puts down acid, alkali and chlorine completely, which illustrate the pollution problem has not been thoroughly resolved in these patents. The present

patent solves the pollution problem of papermaking thoroughly. The invention gets rid of the problem of strong acid, strong alkali, chloride and anthraquinone in pulping process, degradation of lignin and bleaching. All wastewater produced by papermaking isn't drained outwards. The invention is a fully closed, self-circling and zero discharge process and completely solves two worldwide problems - materials shortage of pulping & papermaking and serious pollution.

Detailed description of the invention

The invention overcomes the current technical shortcomings and provides a close-loop, self-cycling, zero discharge, clean oxidizing pulping technology and process.

Clean pulping process and preparation method of the invention are carried out by undermentioned technical projects. The character of the invention is that materials of the clean pulping process and the preparation method are non-wood and wood. Preparation of the pulp can be finished according to undermentioned processes.

(A) Pretreatment of raw materials.

(B) Above materials are oxidizing dipped in water that contains active oxygen A and cellulose preserver that is made of metal ions and metal ion ligands.

(C) The dipped oxidizing materials are grinded in turn by the active oxygen A and active oxygen B.

(D) Concentrate and beating.

In accordance with the present invention, the active oxygen A is selected from O_2 , H_2O_2 , and one or two free radicals generated from O_2 , H_2O_2 . The active oxygen B is selected from O_3 , 1O_2 (singlet oxygen), $O_2^-/HOO\cdot$ (superoxide anion radical) and one or multiform free radicals generated from O_3 , 1O_2 , $O_2^-/HOO\cdot$ in water in which organic

solvent exists.

In accordance with the present invention, the organic solvent, for example, is DMSO or oxalic acid.

A kind of pulp is obtained by above process.

In above clean pulping method, the non-wood materials such as full cotton stalk includes cotton bast, cotton stem, cotton stalk root and full cotton holocellulose, cellulose and hemicellulose of valvular cotton, cotton short linter, cotton dregs, cottonseed, a kind of lignin or two or multi-kinds of their compounds. The described wood fiber includes soft wood and hard wood such as Masson pine, longitudinal white pine, David poplar, fast-growing poplar, birch and so on.

In accordance with the invention, the metal ions are selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Si^{2+} and two or multi-kinds of their compounds. The metallic ion ligands include DMD, DTPA, EDTA, alkyl-sulfonic acid sodium, poly-oxyethyl-enabkylether and two or multi-kinds of their compounds.

In accordance with the invention, dosage of the metal ions is between 1-1000ppm.

In accordance with the invention, the oxidizing dipping treatment is carried out in acidic condition whose pH is between 1-4, and the best pH is between 1.5-2.5.

In accordance with the invention, the grinding treatment is carried out in acidic condition whose pH is between 1-4, and the best pH is between 2.5-3.8.

In accordance with the invention, the acidic condition can be obtained by active oxygen of the invention (such as $HOO \cdot$) and also can be obtained by pH regulator.

In accordance with the invention, the concentration of active oxygen A in above materials is 0.01-2.0wt%, the concentration of active oxygen B in above materials is

0.1-50umol/L.

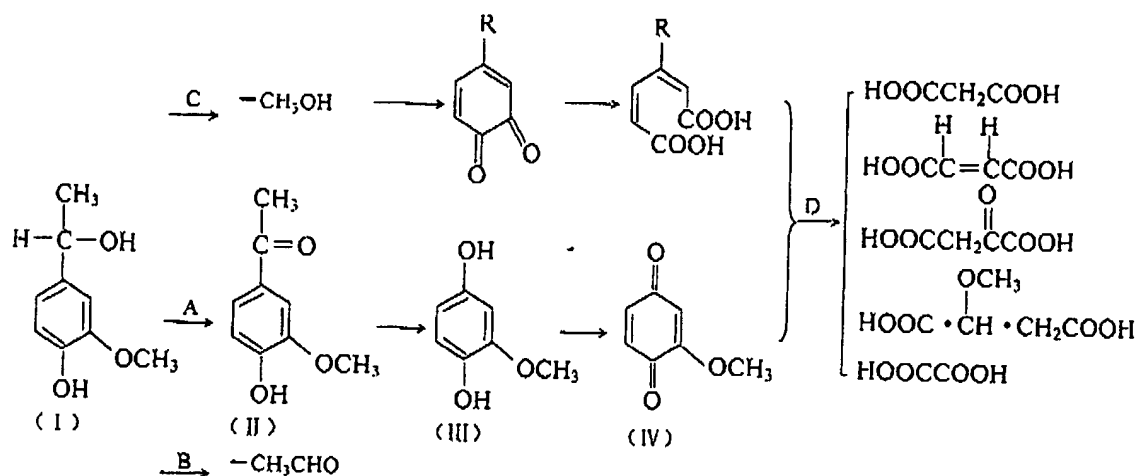
A kind of method as stated above has undermentioned characters and advantages: (A) The active oxygen is dropped into the disc refiner, in which heat energy is generated through the rotation of the disc, and the energy is transferred into the materials for reaction, then the fiber is separated from the intercellular space. (B) With cooperation of the active oxygen A and B, the chromophoric group (α , β -aldehyde or ketone group) in the lignin is transformed into non-color group (the carboxylic acid or binary acid). (C) Self-cycling: All water in the process from the pretreatment of raw materials till the delivery of it to the oxidation reactor is divided into two parts to accomplish the self-cycling in the process. One is the water from the process of materials cleaning pretreatment. It is purified by centrifugal cleaning and the solid sediments in it are taken away. The pulps are sent to the common beating process. Water generated in the process is cycled into purification pool. 0.1%-0.15% ozonizer and acticarbon nutsch filter are installed in the purification pool to decolor the water. The water contains oxygen free radical and it is pumped into the cycling water system. The other is the water from the oxidizing process. After cleaned with centrifugal cleaner and then is concentrated with common decker, the pulp is sent to the tank for papermaking. The produced water is filtrated and placed in the water-purifying tank for self-cycling. The purified water is pumped into materials cleaning system, oxygen dipping system, oxygen grinding system and filtrating system for recycling use.

In accordance with the present invention, it takes advantage of active oxygen free radicals generated by oxidation-reduction reaction of molecular oxygen in reactor to transform and separate lignin, and to change chromophoric group in the intercellular space and obtain paper pulp. The conventional pulping technologies that use harmful polluting chemicals such as acid, alkaline, chlorine, anthraquinone and so on are

basically changed in the present invention. The cooking and bleaching process, generating severe pollution, can be avoided. The abundant yearly grown fiber materials can be utilized in this process and water and energy can be saved. As a result, the cost of production can be saved.

In accordance with the invention, the active oxygen is added in the materials and high-concentration defibrator generates grinding heat reaction by grinding, which is used to change lignin's chromophore of intercellular space. Because the special free radicals formed by three oxygen atoms of molecule oxygen has strong attack power and internal nucleophilic attack power, the electrophilic reaction occurs between special free radicals and lignin. The lignin structural element phenyl and exocyclic big σ -bond are broken, and then lignin is degraded and dissolved. The chromophore of lignin is changed or decomposed into low-molecular, then forms achromictintless monolarboxylic acid or binary carboxylic acid.

Equations are as follows:



The invention also includes the pulp made by above process.

Process of the invention is described concretely as follows:

The character of the invention is that materials of the cleaning pulping process and the preparation method is non-wood and wood. Preparation of the pulp can be finished according to undermentioned processes.

(A) Pretreatment of raw materials.

(B) Above materials is dipped in the active oxygen A and cellulose preserver that is made of metal ions and metal ion ligands.

(C) The dipped oxidizing materials is grinded in turn by the active oxygen A and active oxygen B.

(D) Concentrate and beating.

In accordance with the present invention, the active oxygen A is selected from O_2 , H_2O_2 , and one or two free radicals generated from O_2 , H_2O_2 . The active oxygen B is selected from O_3 , 1O_2 (singlet oxygen), $O_2^-/HOO\cdot$ (superoxide anion radical) and one or multi-free radicals generated from O_3 , 1O_2 , $O_2^-/HOO\cdot$ in water in which organic solvent exists.

Active oxygen can be obtained when O_2 passes through process radiator in which the oxidation-reduction reaction can occur and the energy is provided, at last water is formed. In the process four electrons are accepted, one oxygen free radical will be generated when one electron is absorbed by O_2 . For instance: hyperoxidized anion free radical is formed when O_2 is reduced by one electron and its equation is: $O_2 + e \rightarrow O_2^-/HOO\cdot$. Hydrogen peroxide is formed when O_2 is reduced by two electrons and its equation is: $O_2 + 2e + 2H^+ \rightarrow H_2O_2$. Hydroxy free radical is formed when O_2 is reduced by three electrons and free radical is formed by reaction of Fe^{2+} and H_2O_2 , which are special free radicals of water treatment and their equations are: $O_2 + 3e + 3H^+ \rightarrow H_2O + \cdot OH$, $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$.

In accordance with the invention, the metal ions are selected from Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Si^{2+} and two or multi-kinds of their compounds and the ions are in the form of salt such as $FeSO_4$, $MgCO_3$ etc. The metallic ion ligands is selected from DMD, DTPA, EDTA, alkyl-sulfonic acid sodium, poly-oxyethyl-enabkylether and two or multi-kinds of their compounds. Together with the metal ion, the metallic ion ligand, hyperoxidized anion free radical ($O_2^-/HOO\cdot$) and H_2O_2 , they form a functional cellulose protection system which can not only protect cellulose but also get rid of silicon.

Pretreatment usually includes removing impurity, shear, fiberization and cleanout with concrete condition.

In accordance with the invention, the oxidizing dipping treatment is carried out in acidic condition whose pH is between 1-4, and the best pH is between 1.5-2.5.

In accordance with the invention, the grinding treatment is carried out in acidic condition whose pH is between 1-4, and the best pH is between 2.5-3.8.

In accordance with the invention, the acidic condition can be obtained by active oxygen of the invention (such as $HOO\cdot$) and also can be obtained by pH regulator.

The ions are usually used in the form of salt and its dosage range is commonly between 1-1000ppm, the best range is between 10-100ppm according to weight of metal ion.

In accordance with the present invention, the non-cooking involves that: the conventional cooking process can be omitted. The active oxygen is dropped into the disc refiner, in which heat energy is generated through the rotation of the disc, and the energy transferred reaction is generated, then the fiber is separated from the intercellular space.

In accordance with the present invention, non-conventional bleaching process involves that: the bleaching process can be omitted. The cooperation of the active oxygen A and B are used in order to transform the chromophoric group in the lignin into non-color group. For example, α , β -aldehyde or ketone group are turned to the carboxylic acid or binary acid.

In accordance with the invention the detailed description of the process in the preferred implemented program is illustrated as follows:

The pretreatment system of the raw materials: This is a cooperation process. In this process, materials are removed legumen, calyces by crushing engine and cut into length of 5cm and thick of 1.5cm. Finally materials whose forming rate is 98% are obtained. Above materials are broken into plush by roller and crushing engine, removed dust and medulla by wind power, removed impurity by cleaner. Water of the cleaner is full closed and circular water. Little active oxygen free radicals and little cellulose preserver (could be brought from market) are left in the water, so active oxygen needn't be added in the pretreatment process. No any drainage is drained in the process of washing materials by circular water, which changes the traditional process with acid washing and alkali washing.

Oxidation reactor system (refer to the application of patent for invention of China: 200310103895.3): The main function is imbjbition, softening and debonding of the materials. Active oxygen in the subacidity water whose pH is 1 to 4 generates superoxide anion radicals ($O_2^-/HOO \cdot$) who have strong penetrability and can penetrate intercellular space directly to occur oxidation reaction. Agitator is installed in the oxidation reactor and the agitator connects outer power plant through the top of the reactor.

The agitator at least has three-process propellers, and its rotating speed can be

controlled. Start the agitator and then in the reactor, positive ions are produced in the water. Materials are softened by cooperation of positive ions, pressure, temperature and shearing stress of the agitator. In the oxidation reactor, catenating layer, pectin, poly pentose are decomposed at the same time, and decolor reactions are occurred by high speed agitating of active oxygen.

With the repeatedly experiments, the best reaction conditions are identified: pH1.5-2.5 and a rotating speed of 40-80 r/s for 40-60min. 0.02-0.1% cellulose preserver that has been prepared is also added. In the reactor, chromophore of material changes from deep yellow to pale white then materials are washed repeatedly and squeezed the water out.

Grinding system: the best choice is disk grinder system that is made of two parts, one is model RL50S disc refiner or high consistency defibrator and the other is oxidation reactor. The process has first refining and second refining. Active oxygen A is used in the first refining and active oxygen B is used in the second refining. The raw materials exported by oxidation dipping system are fed to refiner by screw feeder continuously and equally, then the materials are dipped by O_3 whose concentration is 1-15umol/L, weight percentage concentration of water 30%, and pH 2.5. Grinding rotating speed is 600-1200 r/s and the gap between the disks is 0.2-0.15mm. In first refining, active oxygen A whose weight percentage concentration is 0.1-1.5 is added in the shower water to mix grind with materials. The materials are softened with grinding, and then the cellulose cladded in the intercellular space is separated. Main function of the grinding thermal reaction is producing heat transfer reaction with confriction of refiner by mix grinding of active oxygen and material. Chromophore of hydrocinnamic alkyl is oxidized by superoxide anion free radicals, dioxygen and hydrogen peroxide. With softening temperature difference of lignin, hemicellulose and cellulose, hydrophilic groups gotten from oxidized exiguous fibers can connect

fundamental chain of cellulose, as a result, yield is augmented to 8-12%. Key of the invention is condition of the process (the detail instruction of the process such as sequence, pH, temperature, dosage of active oxygen, time, rotating speed, pressure and pulp concentration).

The process has first refining and second refining. slag grinding can be grinded and screened repeatedly after screening. In cleaner disposal process, edible citric acid whose weight percentage concentration is 0.12 and hydroxylamine whose weight percentage concentration is 0.01 are added and sprinkled to prevent dandy worm and oxidative stain. According to routine beating process, the pulp is original material with yield 76% and ISO whiteness 52-65. The process described above can be applied in the village and township enterprises in the area with abundant raw materials. And the coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

The raw materials are fed to refiner continuously and equally. In the first refining process O_2 (weight percentage concentration is 0.1) and H_2O_2 (weight percentage concentration is 1.5) prepared in advance are added to pulp in 1:0.12-0.15 (according to weight ratio) and mixed with pulp in refiner at 60-80°C, pH2.5-3.8 and 12-15% consistency. The rotating speed of which is 1300 r/s and the gap between the disks is 0.15-0.1mm. The pulp whiteness can be 60—75°. In the secondary refining process O_3 (concentration is 10 μ mol/L) and/or superoxide anion radicals ($O_2^-/HOO\cdot$) (concentration is 10 μ mol/L) and/or singlet oxygen (1O_2) (concentration is 10 μ mol/L) are added and mixed with pulp at 80-100°C, pH2.5-3.8, 12-15% pulp consistency and 0.3-0.6Mpa. The rotating speed of refiner disc is 1300 r/s and the gap is 0.15-0.1mm. After 0.5-1h, the ISO whiteness can reach to 75-86°. The pulp is sent into the conventional screening process for fine screening. The refined pulp is sent into the centrifugal cleaning process before it is condensed with decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can

be processed again according to the process described above and pulp yield is 75%.

Comparing with current technology, method of the invention has advantages as follows: It is practically a process which involves a method with close-loop, self-cycling, non-acid, non-alkali, non-chlorine, non-anthraquinone, non-cooking, non-bleaching, non-draining and non-pollution. The method has characters of saving energy, saving water and clean pulping and it solves pollution of papermaking completely, utilizes the resource of agriculture and forest, and protects the environment. In accordance with the present invention, the fully closed, self-cycling, zero discharge refers to: All water in the process from the pretreatment of raw materials till the delivery of it to the oxidation reactor is divided into two parts to accomplish the self-cycling in the process. One is the water from the process of materials cleaning pretreatment. It is purified by centrifugal cleaning and the solid sediments in it are taken away. The pulps are sent to the common beating process. Water generated in the process is cycled into purification pool. 0.1%-0.15% ozonizer and acticarbon nutsch filter are installed in the purification pool to decolor the water. The water contains oxygen free radical and it is pumped into the cycling water system. The other is the water from the oxidizing process. After cleaned with centrifugal cleaner and then is concentrated with common decker, the pulp is sent to the tank for papermaking. The produced water is filtrated and placed in the water-purifying tank for self-cycling. The purified water is pumped into materials cleaning system, oxygen dipping system, oxygen grinding system and filtrating system for recycling use. No any gas or black liquor is drained in the process. The mixed solid residue only occupied 12%-22% of the materials. This process is pollution-free and the residue can be sent to bio-oxidation treatment tank.

Caption of the drawing:

The flow sheet of this invention that is a fully closed, self-cycling, zero discharge and clean pulping process is illustrated in Figure 1.

EXAMPLE

Undermentioned examples are farther description of the invention. These examples are only used to describe the invention, not used to limit the conceptual framework of the invention.

EXAMPLE I

100kg full cotton stalks are removed legumen, calyces by crushing engine and cut into length of 5cm and thick of 1.5cm. Finally materials with forming rate 98% are obtained. Above materials are broken into plush by roller and crushing engine, removed dust and medulla by wind power, removed impurity by screening, washed by circular water before the materials is transported to the oxidation reactor (auto agitator is installed in the reactor) by screw feeder. The reaction conditions are at 60°C, pH2.5, rotating speed of 60 r/s and MgCO_3 0.02 kg, and bimethyl-bioxirane (DMD) 0.01 kg is added. After 0.5h H_2O_2 solution with weight percentage concentration 0.2 is added. Then the rotating speed becomes 80 r/s and temperature is 80°C. After 1h, impregnating softness number of the materials in the reactor is 98%. The materials change from deep yellow to pale white and accord with ISO whiteness 48-52° (hereinafter it is called whiteness or ISO whiteness for short). Above materials are washed repeatedly and dewatered to concentrate, and weight percentage concentration of the water is 30%. H_2O_2 solution is added in the material, and weight percentage concentration of H_2O_2 in the material is 0.2. The material is fed to refiner continuously and equally to be grinded. The rotating speed of refiner disc is 600-1200 r/s and the gap between the disks is 0.2-0.15mm. slag grinding can be grinded and

screened repeatedly after screening. In disposal process of cleaner, edible citric acid with weight percentage concentration 0.12 and hydroxylamine with weight percentage concentration 0.01 are added. According to routine beating process, the pulp is original material that yield is 76% and ISO whiteness is 52-65. The process described above can be applied in the village and township enterprises in the area with abundant raw materials. And the coarse pulp products can be supplied sufficiently to the consolidation pulp mills.

EXAMPLE II

In accordance with EXAMPLE I, 100kg raw materials are fed to refiner continuously and equally. In the first refining process H_2O_2 (weight percentage concentration is 1.5) prepared in advance are added to pulp in 1:0.12 (according to weight ratio) and mixed with pulp in refiner at 60°C, pH3.8 and 12-15% consistency. The rotating speed of refiner is 1300 r/s and the gap between the disks is 0.15-0.1mm. The pulp whiteness can be 60-75°. In the secondary refining process O_3 (concentration is 10umol/L) is added and mixed with pulp at 80°C, pH3.8, 12-15% pulp consistency and pressure 0.4Mpa. The rotating speed of refiner disc is 1300 r/s and the gap is 0.1mm. After 0.5-1h, the ISO whiteness can reach to 75-86°. The pulp is sent into the conventional screening process for fine screening. The refined pulp is sent into the centrifugal cleaning process before it is condensed with decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield is 75%.

EXAMPLE III

Original materials are obtained by the procedure as conducted for example I, except that $MgSO_4$ substitutes for $MgCO_3$ at the same dosage.

EXAMPLE IV

The procedure as conducted for example II, except that superoxide anion radicals ($O_2^-/HOO \cdot$) whose concentration is 10 μ mol/L substitutes for O_3 whose concentration is 10 μ mol/L.

EXAMPLE V

100kg poplar pieces are broken into plush by roller and crushing engine, removed dust and impurity by wind power, washed by circular water before the materials are transported to the oxidation reactor (auto agitator is installed in the reactor) by screw feeder. The reaction conditions are at 60°C, pH2.5, rotating speed of 60 r/s and $MgSO_4$ 0.015kg and bimethyl-bioxirane (DMD) 0.01 kg are added. After 0.5h H_2O_2 solution whose weight percentage concentration is 0.2 is added. Then the rotating speed becomes 80 r/s and temperature is 100°C. After 1h, impregnating softness number of the materials in the reactor is 98%. The materials change from deep yellow to pale white and ISO whiteness is 48-52°. Above materials is washed repeatedly and dewatered to concentrate, and weight percentage concentration of the water is 30%. O_2 and H_2O_2 solution is added in the material, and weight percentage concentration of H_2O_2 in the materials is 0.25. The materials are fed to refiner continuously and equally to be grinded. The rotating speed of refiner disc is 600-1200 r/s and the gap between the disks is 0.2-0.15mm. Slag grinding can be grinded and screened repeatedly after screening. In cleaner disposal process, edible citric acid whose weight percentage concentration is 0.12 and N, N-dialkyl hydroxylamine whose weight percentage concentration is 0.01 are added. According to routine beating process, the pulp is original material whose yield is 76% and ISO whiteness is 52-65.

EXAMPLE VI

100kg poplar pieces are fed to refiner continuously and equally. In the first refining process, compound oxygen made of H_2O_2 (weight percentage concentration is 1.5) and O_2 (weight percentage concentration is 0.1) prepared in advance are added to pulp in 1:0.15 (according to weight ratio) and mixed with pulp in refiner at $60^\circ C$, pH3.8 and 12-15% consistency. The rotating speed of refiner is 1300 r/s and the gap between the disks is 0.15-0.1mm. The pulp whiteness can be $60-75^\circ$. In the secondary refining process superoxide anion radicals ($O_2^-/HOO \cdot$) (concentration is 10umol/L) is added and mixed with pulp at $80^\circ C$, pH3.8, 12-15% pulp consistency and 0.4Mpa. The rotating speed of refiner disc is 1300 r/s and the gap is 0.1mm. After 0.5-1h, the ISO whiteness can reach to $75-86^\circ$. The pulp is sent into the conventional screening process for fine screening. The refined pulp is sent into the centrifugal cleaning process before it is condensed with decker, beaten, and then sent into the storage process. When higher whiteness is required, the pulp can be processed again according to the process described above and pulp yield is 75%.

EXAMPLE VII

Original materials are obtained by the procedure as conducted for example V, except that ETPA substitute for DMD at the same dosage.

EXAMPLE VIII

The procedure as conducted for example VI, except that singlet oxygen (1O_2) whose concentration is 10umol/L and O_3 whose concentration is 10umol/L substitute for superoxide anion radicals ($O_2^-/HOO \cdot$) whose concentration is 10umol/L. In accordance with the present invention, there is provided a non-cooking, non-conventional bleaching, fully closed, self-cycling and active oxygen mixed refining process. The unexpected chemicals such as strong chlorine, strong acid,

strong alkaline are not employed. According to the market demands, the enterprise can produce various types of middle or high quality pulp.

The test results of clean oxidizing pulp:

Pilot product, namely pulp of full cotton stalk, mulberry tree, poplar and the full cotton stalk screen pulp, was tested by Tianjin Science and Technology University. The results are shown in the testing report in detail (table 5). It is indicated that bio-oxidation pulping technology can be applied to both wood and non-wood materials, for example, full cotton stalk, the agriculture residue, can be utilized as raw materials for pulping.

Testing report and national sulfite bleach pulping contrast table are produced by Tianjin Science and Technology University at Nov 12, 2003. Please refer to table 3.

Table 3 property comparison of bio-oxidation pulp and conventional CMP

Index	GB Standard Of BSP	Upland Cotton Pre-Screene d Pulp	Upland Cotton Screened Pulp	Mulberry Pre-Screene d Pulp	Poplar Pre-Screene d Pulp
Fiber length(mm)	0. 50	0. 51	0. 65	0. 47	0. 55
Degree of beating (°SR)	45	59	51. 5	58	62
Basis weight (g/ m ²)	58. 2	58. 2	60. 0	59. 0	57. 5
density (g/cm ³)	3. 3	0. 33	0. 32	0. 33	0. 32
Breaking length	3. 2	3. 81	3. 44	3. 44	3. 07

(Km)					
Tear index (mNm ² /g)	2.8	2.9	3.4	2.9	2.5
Burst index (KPam ² /g)	1.5	1.9	1.5	1.7	1.4
Brightness (%ISO)	82.0	68.69	71.58	70.87	75.17
Opacity (%)	88.1	95.91	93.91	96.05	94.07